# NON-THERMAL PLASMA-ASSISTED COMBUSTION RESEARCH AT LOS ALAMOS*

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*Abstract*

The application of electric fields to flames has been reported as early as 1814, was applied to furnaces in the 1920's and developed into several applications in the last half of the 20th Century. When the electric field strength is sufficient to cause electrical breakdown of a fuel or fuel/air mixture, plasma effects will dominate. Plasma effects can increase electron and ion temperatures and promote combustion through the formation of 'active' species (such as free radicals) or the dissociation of fuel molecules into smaller, easily-combusted fragments [1].

Plasma-assisted combustion (PAC) is now a timely research topic worldwide [2], pointing to more efficient fossil-fuel usage, conversion of low-grade fuels into higher-grade fuels, and pollution reduction through ultra-lean burn combustion. Our work focuses on non-thermal ('cold') plasmas (NTPs), particularly for enhancing combustion stability, efficiency, and reducing undesirable emissions. This is in contrast to thermal ("hot") plasmas.

Here we discuss representative PAC experiments focused on combustion stability, efficiency, and pollution reduction. Our work has been mainly carried out with silent electrical discharges (also called dielectric-barrier discharges - DBDs) – where only the fuel is activated. DBDs are convenient sources for producing atmospheric-pressure NTPs. Using DBD devices, we have tested hydrocarbon fuel activation/conversion systems that fragment hydrocarbons into smaller compounds, increase flame speed, stabilize flames, and operate in very lean burn regimes (where the production of pollutants such as $NO_x$ and CO are expected to decrease). Experiments have been carried out with methane, ethane, propane and butane, as well as the gasoline surrogate liquid iso-octane.

## I. BACKGROUND

### *A. Conceptual Framework*

Conventional combustion of hydrocarbons in air typically begins with spark ignition - a spark thermally decomposes hydrocarbon and air molecules to produce free radicals and other reactive species. Burning then continues by subsequent reactions of the reactive species created by combustion-generated heat. The overall combustion rate is usually determined by how efficiently new reactive species are generated in the propagating flame front. However, this self-generation of reactive species is sometimes insufficient to sustain combustion, particularly under lean-burn conditions.

NTP 'activation' does not rely on self-generation of reactive species. Two possible mechanisms for fuel cracking and fuel activation (creation of more reactive species) exist. One is based on electron-impact processes, such as dissociation, dissociative ionization, vibrational excitation, and electronic excitation of the parent fuel molecule, which produces molecular fragments, radicals, or excited states relevant to the promotion of combustion reactions. Another mechanism is ion-molecule reactions, in which ions created by electron impact react with neutral gas species and produce species which can promote combustion reactions.

### *B. Sample Electron Impact Reactions*

Some possible electron impact dissociation reactions for the example hydrocarbon ethane ($C_2H_6$, structure $CH_3$-$CH_3$) are illustrated below. The most probable reactions for 'cracking' or fragmentation into smaller molecules are cleavage of single carbon-carbon bonds, producing methyl ($CH_3$) radicals; or the more energy-intensive cleavages of carbon-hydrogen bonds, which can produce CH• radicals, methyl radicals, methylene/carbene radicals ($H_2C$:), and hydrogen radicals (H•), or electronic excitations producing excited-state molecule and molecular hydrogen ($H_2$).

$$e + C_2H_6 \rightarrow 2CH_3\bullet + e$$
$$e + C_2H_6 \rightarrow H_3\bullet + CH_2: + H\bullet + e$$
$$e + C_2H_6 \rightarrow CH\bullet + CH_3\bullet + H_2 + e$$
$$e + C_2H_6 \rightarrow C_2H_4^* + H_2 + e$$

From the above reactions, we see that the greater the degree of cracking, the higher the concentration of reactive species and, in general, the greater the species reactivity (e.g., carbenes). The more the fuel is cracked/activated, the faster the combustion rate, because smaller species normally burn faster. Under electron impact, hydocarnons are also likely to be ionized into

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14. ABSTRACT
**The application of electric fields to flames has been reported as early as 1814, was applied to furnaces in the 1920s and developed into several applications in the last half of the 20th Century. When the electric field strength is sufficient to cause electrical breakdown of a fuel or fuel/air mixture, plasma effects will dominate. Plasma effects can increase electron and ion temperatures and promote combustion through the formation of active species (such as free radicals) or the dissociation of fuel molecules into smaller, easily-combusted fragments [1]. Plasma-assisted combustion (PAC) is now a timely research topic worldwide [2], pointing to more efficient fossil-fuel usage, conversion of low-grade fuels into higher-grade fuels, and pollution reduction through ultralean burn combustion. Our work focuses on non-thermal (cold) plasmas (NTPs), particularly for enhancing combustion stability, efficiency, and reducing undesirable emissions. This is in contrast to thermal (hot) plasmas**

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multiple species and these species then further fragment into smaller molecular ions.

$e + C_2H_6 \rightarrow$ Multiple ion species,
$C_xH^+_{2x+2} \rightarrow C_mH_n+ + M,$

where x, m, and n are integers and M is a neutral molecule. When ionic recombination and/or charge transfer reactions follow dissociative ionization, smaller, more easily-combusted molecular fragments result.

### *C. Sample Secondary Reactions*

Radicals formed in the above processes can then further dissociate ethane, or its decomposition products, to yield additional fragments and active species, as shown below.

$H\bullet + C_2H_6 \rightarrow C_2H_5\bullet + H_2$ or $CH_3\bullet + CH_4$
$H\bullet + C_2H_2 \rightarrow C_2H_3$ or $C_2H + H_2$
$H\bullet + C_2H_4 \rightarrow C_2H_5\bullet$ or $C_2H_3 + H_2$
$H\bullet + C_2H_5\bullet \rightarrow C_2H_4 + H_2$ or $2CH_3\bullet$
$CH\bullet + CH_4 \rightarrow C_2H_4 + H\bullet$
$CH\bullet + C_2H_4 \rightarrow C_3H_2 + H_2 + H\bullet$ or $C_2H_2 + CH_3\bullet$
$CH\bullet + C_2H_6 \rightarrow$ Products (e.g., $C_2H_2 + CH_4 + H\bullet$)
$CH_2: + C_2H_6 \rightarrow C_3H_8$ or $CH_3\bullet + C_2H_5\bullet$
$CH_3\bullet + C_2H_6 \rightarrow CH_4 + C_2H_5\bullet$

The unstable, excited-state ethylene molecule can then further decompose into acetylene ($C_2H_2$) and molecular hydrogen ($H_2$).

$C_2H_4^* \rightarrow C_2H_2 + H_2$

Another mechanism considered for fragmentation or active species formation is ion-molecule reactions which typically involve charge transfer reactions with negative oxygen ions (formed in electric discharges in air) to form hydroxyl (OH) radicals, which can promote combustion chain reactions.

The detection and identification of radical species arising from the decomposition of pure hydrocarbons is a difficult task and such studies have been sparsely reported in the literature. More study in this area is needed. The results of experiments, followed by plasma chemistry modeling and further diagnostics of stable and intermediate species will be needed to lend further insight into the dominant processes of plasma-assisted combustion (PAC).

## II. EXPERIMENTS

### *A. General Experimental Setup*

Figure 1 shows a block diagram of a typical experimental setup for our two types of PAC investigations: (1) plasma decomposition/'cracking' of hydrocarbon gases, and (2) properties of flames when hydrocarbon fuels are 'activated' by a DBD-generated NTP.

Both types of experiments use similar diagnostic, analytical-chemistry instruments.

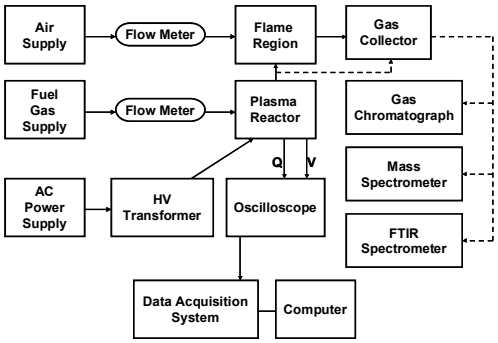


**Fig. 1:** Block diagram of typical DBD, non-equilibrium plasma-assisted combustion experimental setup.

The dashed line from the reactor shows the route of plasma-activated gases under non-combustion conditions ('cracking'), while the solid line to the flame region refers to flame studies. We emphasize that in our experiments the air is not activated – only the fuel is treated by the plasma reactor. When flames are employed, air is mixed with the fuel gas after it is activated by the plasma.

### *B. Plasma Reactors & Instruments*

In our usual experiments, we employ a coaxial, cylindrical DBD reactor that processes pure hydrocarbon gas at local-Los Alamos, ambient pressure (77.3 kPa, because of the Laboratory's altitude of ~ 2200 m) and near-ambient temperature. DBDs, being sources of NTPs, do not considerably raise the process gas temperature – the deposited electrical energy mainly goes into chemical decomposition and molecular excitation – not heat/enthalpy. We used two different types of DBD reactors for our investigations: one for cracking and flame propagation (speed) observations and another for lean-burn flame operation and exhaust-gas species determination.

An artist's rendering of a typical coaxial reactor used for cracking experiments is shown in Figure 2. A similar reactor is used for flame studies, but using an exhaust-gas collector displaced above the top of the reactor (where a flame appears). In both reactors, a grounded tubular inner electrode (diameter 9.5 mm) is centered inside a fused-silica, dielectric-barrier tube (inner diameter 13 mm and wall thickness 3 mm). Hydrocarbon gas flows through the annular space (1.75 mm gas gap) between the inner electrode and the inside of the fused silica tube. The fused-silica tube is surrounded by a 120-mm high, cylindrical, metal outer electrode (a copper-mesh screen bounded by copper 'corona' rings), connected to a high-voltage, AC transformer. For lean-burn flame operation and flame exhaust-gas species determination, coaxial reactors, similar to Figure 2, but using a solid outer conductor and an alumina-ceramic dielectric tube, were

employed. In these cases, air flows through the inner, 'ground' electrode tube and then mixes with the NTP-activated hydrocarbon gas that flows in the annular space.

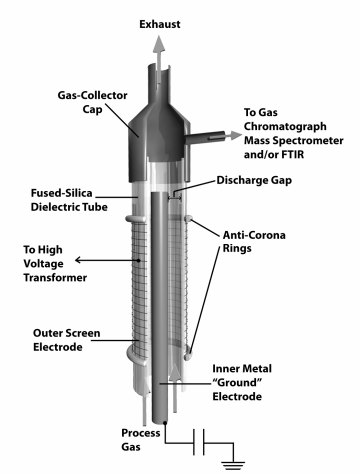


**Fig. 2:** Illustration of DBD reactor for 'cracking' studies.

Electrical power is applied to the hydrocarbon-gas gap (by a high-voltage source connected to the outer electrode) and, when the electrical breakdown voltage is exceeded, plasma is formed in the gas, thus activating and decomposing it. Figure 3 shows a circuit schematic diagram for the setup.

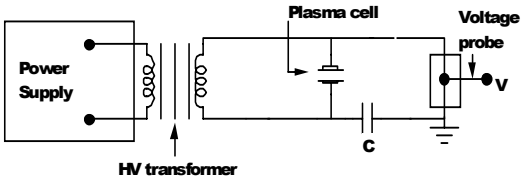


**Fig. 3:** Circuit schematic diagram for DBD reactor setup.

The stable decomposition products or flame-exhaust products can be detected with a gas chromatograph, mass spectrometer, or FTIR. In the near future, experiments will be carried out to determine the intermediate (unstable) reaction products.

The electrical power supply consists of a function generator, which supplies a low-voltage sinusoidal signal to an AC amplifier, which drives a high-voltage transformer. This produces a voltage of order 7 - 15 kV on the outer, metal-mesh or solid electrode. For gas gaps ~ 1.5 mm, ambient pressure of ~ 0.77 atm, and ambient temperature of about 23 C, the breakdown reduced electric field in the gas gap is approximately E/N = 130 Td for methane, 163 Td for ethane, and 105 Td for propane. Two different transformers are normally employed to drive the DBD reactor: low-frequency (10's Hz – 1 kHz) and higher-frequency (5 – 20 kHz). The applied frequency is tuned to match the impedance of the DBD reactor, depending on the gas employed. The reactor voltage is monitored with a high-voltage probe. The charge transferred through the reactor is monitored by measuring the voltage on a capacitor connected in series to the transformer ground. These signals are delivered to an oscilloscope, which interfaces to a data acquisition/data processing computer.

The power deposited into the plasma is determined from these two measured voltages, using Lissajous-diagram techniques (charge-voltage plot), as originally developed by Manley in 1943 [3] and a computer data-analysis program. The plasma specific energy ε (energy per unit volume) is obtained by dividing the deposited electrical power P by the process gas flow rate Q

$$\varepsilon = P/Q$$

The specific energy is usually expressed in units of joules per liter (J/L).

### *C. Experimental Results*

In the limited space of this paper, we can only provide brief summaries of our experimental results. Overall, we have demonstrated the decomposition ('cracking') of gaseous hydrocarbons into smaller fragments, been able to extend the blowout limits of plasma-activated hydrocarbon-air flames to very lean-burn regimes, increased flame speeds, and have observed more complete combustion in flames.

*1) Decomposition/Cracking Experiments*

Experiments were conducted on the cracking of methane, ethane, propane, and butane in the absence of a flame, using a closed coaxial reactor (like Figure 2). Plasma-treated effluent gas was collected at the end of the reactor and then sent to a mass spectrometer (MS) for analysis. For both propane and butane, there was a substantial increase in the normalized MS signal for the lower mass peaks M = 15, 26, 27, and 29; but only M = 15 and 16 showed a significant increase for methane.

*2) Lean-Burn/Blowout Experiments*

The influence of plasma excitation on the blowout limit of an activated-propane/air flame (i.e., ultra-lean-burn conditions) is described in detail in [4]; results are summarized here. For these studies, the experimental setup shown in Figure 1 and a ceramic-dielectric, coaxial DBD reactor were used. As in the reactor of Figure 2, in the lean-burn reactor, air flows through the 'ground' tubular inner electrode and propane flows through the annular gap between the inner electrode and an alumina ceramic tube (substitute ceramic for quartz, as in Figure 2). The ceramic tube is surrounded by a cylindrical, solid metal outer electrode (as opposed to the screen electrode in Figure 2), which is powered by a HV AC transformer. Power is applied to the propane but not the air, activating the fuel alone (in the annular region between the center-

ground electrode and the ceramic-dielectric tube). This activated fuel is then mixed with air, coming through the center ground-tube and then ignited at the top of a short mixing region.

Blowout tests were conducted by holding the propane flow (through the annular region) constant and increasing the air flow rate (through the inner ground-tube) until the flame blew out. The blowout air flow rate is an indicator of flame stability, and a high blowout air flow rate shows that combustion continues to occur under lean-burn conditions. Most notably, the strongest plasma effect is increased stability at large air flows [4]. The minimum blowout air flow rates vs propane flow of an inverse, partially-premixed flame for propane flow rates between 0.2 and 0.8 std lit/min were obtained. The results are parameterized according to a standard combustion metric, the equivalence ratio $\phi$, for propane-air combustion.

$$\phi = 15.6 \cdot (Q_p/Q_a) \cdot (\rho_p/\rho_a) \,,$$

where $Q_p$ and $Q_a$ are the propane and air volume flow rates and $\rho_p$ and $\rho_a$ are the densities of propane and air, respectively. In the absence of plasma, the blowout limit of a propane flame increases with the propane flow rate and begins to saturate at 0.6 std lit/min propane. When a 10-W plasma is applied to the fuel, the blowout limit shows a large increase for low propane flow (low equivalence ratio).

*3) Flame-Speed Experiments*

Here, a reactor similar to that of Figure 2 was used. The ends of the electrodes and the end of the quartz tube were separated by a 6-cm mixing region (Figure 4: marks 1, 2), sufficient to eliminate direct effects of the electric field on the flame. The air- and propane-flow rates were set to fix $\phi = 1.58$ (where burning is relatively complete).

Figure 4a shows a propane-air flame in the absence of plasma. The application of a low-power, 4 W plasma (Figure 4b), improves the flame symmetry, a marker of stability. In both 4a and 4b, the flame propagates upward only, because the flame propagation rate is insufficient to overcome the upward flow of the propane-air mixture. As more power (specific energy) is applied to the plasma, downward propagation becomes increasingly pronounced (Figure 4c). The changes in the flame's ability to propagate downward suggest that the flame-propagation rate increases with plasma power (specific energy) [5].

Experiments comparing methane, propane, and butane flame speeds under the influence of an NTP showed that the flame speed increases in the order butane > propane > methane.

Other experiments, not described here, showed enhanced consumption of propane in a flame when the propane was activated by an NTP [6].

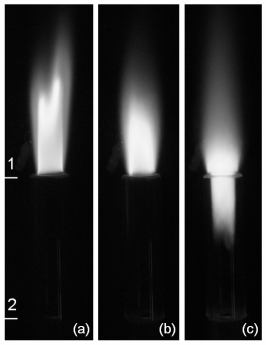


**Fig. 4:** Photos showing an increase in flame propagation speed under the influence of a DBD-driven plasma (propane activated by plasma before mixing with air and combusted).
a: No plasma, b: 4W, c: 10W. [4]

## III. SUMMARY

The potential applications of NTPs to combustion are broad, ranging from ignition to flame stabilization, to pollution reduction and increased fuel efficiency. Here, we have described some proof-of-principle experiments showing promising results for gaseous fuels. However, more research and development is needed to understand the basic combustion-enhancement mechanisms and optimize the process. If applications to other fuels (e.g., gasoline, diesel, jet fuel) are successful, NTP-assisted combustion may favorably impact global fuel usage.

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